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A model for Electron Nuclear Dynamics of a Monatomic Chain

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ABSTRACT

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I. Introduction

The recently developed Electron Nuclear Dynamics (END) method [1-10] offers promising opportunities towards an integrated understanding of electronic and nuclear motion and their coupling. Instead of the traditional separation of that problem into basically three steps — the calculation of a potential energy surface, the determination of an analytical representation of that surface, and the dynamics on the surface — the END method attacks the problem in one step. This has both conceptual and computational advantages. The general framework of the END is a variational approach towards the solution of the time-dependent Schrödinger equation for all the particles of interest in the system.

Employing the time-dependent variational principle (TDVP) [11, 12], a set of first-order coupled differential equations for parameters characterizing a time-dependent state vector is derived. These time dependent parameters define an approximate solution of the time dependent Schrödinger equation for the system under study. The parameters can be of "electronic" type, such as coefficients of basis functions in molecular or crystal orbitals, or of "nuclear" type, i.e. characterizing the state vectors for the nuclei. The method has the flexibility to accommodate either a quantum mechanical or a classical treatment of the nuclei. When the nuclei are treated as classical particles the nuclear coordinates and momenta are the parameters that evolve in time.

The END theory can be viewed as a general approach to study time evolution, and thus also, through appropriate Fourier transforms, spectra in general scattering or bound state problems. A particular choice of the form of state vector or wavefunction and associated basis sets yields a certain realization of END or in other words a particular model within the END framework. When parameters are independent of time the equations of motion reduce to the extremum conditions of the time-independent variational principle. The computer program ENDyne [13], which implements the theory, can thus also be used for geometry optimization calculations. With frozen nuclei the dynamical equations can accomplish wavefunction optimization and in general simultaneous geometry and wavefunction optimization.

The simplest possible approximation of END theory involves classical nuclei and a single determinantal wavefunction for the electrons. The latter choice may seem somewhat restricted, however, with appropriate choice of wavefunction parameters the determinantal wavefunction can be given the form of a *coherent state*. In this so called Thouless form [14] of the determinant the parameters that determine the degree of mixing of the basis functions are chosen in such a way that as they change in time all possible determinantal states in the given basis can in principle be accessed. The dynamical spin orbitals that make up the Thouless determinant are complex nonorthogonal functions, which can permit general spin orbitals of various kinds in line with the work of Fukutome [15]. The computer code ENDyne is implemented at this simplest level of approximation. However, the theory has been worked out for a general multiconfigurational state vector for the electrons [6] and for a wave packet treatment of the nuclei [5].

Most of the applications of END carried out so far are concerned with reactive collision problems involving small species, and in particular electron transfer reactions for such systems. Modifications necessary for larger systems including extended polymeric systems are under way. The present paper employs the END to develop a consistent procedure to describe the coupling between electronic and nuclear motion in extended systems. This will bring two areas together

which have so far often been treated separately, namely lattice dynamics and band theory. Only small vibrations of the nuclei (ion cores) around their equilibrium positions are considered in the present model.

The purpose of the present paper is to identify in some detail and address a number of problems connected with the application of the END method to an extended system. The long range aspect of the Coulomb interaction becomes a particularly important issue in the treatment of extended systems, with wavefunctions that must extend throughout the system [16]. Both in traditional lattice dynamics and band theory the associated problems are well-known [17], and it is essential to keep them in mind when developing a new approach.

Instead of attempting directly a full *ab initio* treatment a model system is discussed where some of the steps in the development can be handled analytically. The Pariser-Parr-Pople (PPP) model [18, 19] was originally developed for incorporating electron-electron interaction in the treatment of π -electron molecular systems. The PPP Hamiltonian [20], which has grown out of the original work, has been applied to a wide range of many-electron problems. It has been applied at several levels of approximation not the least to the treatment of polymers (see for instance [21] and [22] and references therein). This PPP Hamiltonian forms the starting point of the present paper. The particular features of the END method and the fact that it considers both nuclear and electronic dynamics requires a careful analysis and specification of the traditional parameters. An essential aspect of the PPP model is that the parameters can be chosen so as to preserve the long range properties of the Coulomb interaction. The energy of the system for a static lattice in this model will therefore be proportional to the number of atoms (the volume) of the system and it is important to study how the energy depends on the small nuclear vibrations around the equilibrium positions. A harmonic approximation in terms of these deviations is therefore natural. A harmonic approximation of the total energy is adopted with respect to the electronic parameters. The model then represents a fully coupled electronic-nuclear problem at the level of the Random Phase Approximation (RPA) or linearized Time-Dependent Hartree Fock (TDHF). This approach has been discussed in general terms in reference [3].

The main part of the paper is planned as follows. The basic END framework is summarized in the next section. In section III a number of problems associated with the treatment of extended systems are reviewed, with particular attention given to the separation of long and short range forces and also to the importance of working with quantities that scale correctly with the size of the system. In section IV the particulars of the chosen model are discussed. The question of how to choose the electronic basis functions for the END treatment is discussed in a separate section. In sections VI, VII, and VIII explicit applications of END to three cases are carried out. First, in order to connect to more traditional treatments, the cases with only nuclear parameters (section VI), and only electronic parameters (section VII) are treated. Then in section VIII the general case is considered with both electronic and nuclear parameters. Finally, the results are summarized and further possible extensions are discussed in the last section.

II. The END equations for a single determinant and classical nuclei.

A lattice, periodic in one dimension, is considered, that consists of M unit cells of length a with one atom per unit cell. Generalization to an arbitrary number of atoms per unit cell

is straightforward. Periodic boundary conditions are imposed so that all wavefunctions satisfy ($\vec{d} = a\vec{e}_x$)

$$\psi(\vec{r} + M\vec{d}) = \psi(\vec{r}). \quad (\text{II.1})$$

The integer m labels the M cells in the Born-von Kármán region (BK) $-M/2 \leq m \leq M/2 - 1$.

The actual nuclear (core) positions are denoted

$$\vec{R}(m) = \vec{m} + \vec{\rho}(m) \quad (\text{II.2})$$

where \vec{m} is a point in cell m defined by the equilibrium position for that nucleus. In other words this is the *anchor point* of the nucleus (core) and $\vec{\rho}(m)$ is the displacement from the equilibrium of that nucleus (core). The presentation is limited to small vibrations around the equilibrium positions so that $\rho \ll R$. The nucleus in cell m has momentum $\vec{P}(m)$. The displacements $\vec{\rho}(m)$ and therefore the nuclear positions, as well as the momenta depend on the time parameter t , while the anchor points \vec{m} are time independent.

The electrons in the system are described by a single determinant built from dynamic spin orbitals ($\xi = (\vec{r}, \zeta)$ with ζ the spin coordinate)

$$\chi_i(\xi) = \psi_i(\xi) + \sum_{j=N+1}^K \psi_j(\xi) z_{ji}(t); \quad 1 \leq i \leq N. \quad (\text{II.3})$$

The rank of the spin orbital basis $\{\psi_i\}$ is K and the first N of the basis spin orbitals make up the so called reference determinant. The time dependent electronic wavefunction is defined as

$$|\mathbf{z}\rangle = \det\{\chi_i(\xi_j)\} \quad (\text{II.4})$$

where \mathbf{z} is used as a collective symbol for all the $N(K-N)$ complex parameters $z_{ji} = z_{ji}(t)$. This form of the determinantal wavefunction has the form of a generalized coherent state [23, 24, 3]. It is unnormalized and the normalization is

$$S(\mathbf{z}^*, \mathbf{z}) = \langle \mathbf{z} | \mathbf{z} \rangle = \det\{1 + \mathbf{z}^\dagger \mathbf{z}\}. \quad (\text{II.5})$$

Classical treatment of the nuclei can be considered as the narrow wavepacket limit of a product of frozen Gaussians. The TDVP is used to arrive at a set of coupled differential equations for the electron nuclear dynamics by making stationary the quantum mechanical action [8]. The dynamical equations can be expressed as

$$\begin{pmatrix} iC & 0 & 0 & 0 \\ 0 & -iC^* & 0 & 0 \\ 0 & 0 & 0 & -1 \\ 0 & 0 & 1 & 0 \end{pmatrix} \begin{pmatrix} \dot{\mathbf{z}} \\ \dot{\mathbf{z}}^* \\ \dot{\mathbf{R}} \\ \dot{\mathbf{P}} \end{pmatrix} = \begin{pmatrix} \partial E / \partial \mathbf{z}^* \\ \partial E / \partial \mathbf{z} \\ \partial E / \partial \mathbf{R} \\ \partial E / \partial \mathbf{P} \end{pmatrix} \quad (\text{II.6})$$

where the dot denotes time differentiation, say $\dot{\mathbf{z}} = d\mathbf{z}/dt$. The dynamical metric has the matrix elements

$$\partial^2 \ln S / \partial z_\alpha^* \partial z_\beta = C_{\alpha\beta} \quad (\text{II.7})$$

and the total energy E is a sum of the electronic energy $\langle \mathbf{z} | H \mathbf{z} \rangle / \langle \mathbf{z} | \mathbf{z} \rangle$ (H being the electronic Hamiltonian), the nuclear kinetic energy, and the nuclear-nuclear repulsion energy.

The integration of this very large set of coupled differential equations in time is a technical problem that has been solved in practice for finite molecular systems. The actual choice of basis functions and electronic parameters \mathbf{z} are discussed in sections V and VII.

III. Special considerations for extended systems

Long and short range potentials

In order to treat an extended system in a meaningful way one cannot simply let the number of nuclei and electrons grow indefinitely. Great care is required in order to insure that the expressions scale correctly with size and that electric neutrality is maintained. This is particularly important since the Coulomb interaction is long range. The final quantities are always expressed per unit volume, per unit cell, per atom, or per electron and thus proper scaling with size is crucial. This must be kept in mind when partitioning the energy or other quantities into partial quantities. Each part must be proportional to M , the number of unit cells.

It is well-known (see e.g. Fetter and Walecka [16]) that transition from a finite to an extended system with Coulomb interactions is extremely sensitive. It may be handled by means of two coupled limiting procedures. One replaces the true Coulomb interaction by a screened interaction

$$e^{-\lambda r}/r. \quad (\text{III.1})$$

When the desired quantities have been calculated one lets the screening constant in the corresponding expressions tend to zero at the same time as the size (the number of unit cells) of the system tends to infinity in such a way that the interaction remains operative throughout the whole system.

Requirements of this type imposed by the physics of the problem also show up in the form of the need for lattice sums to be convergent. The partitioning of the total energy into three parts (apart from the nuclear kinetic energy, which by itself is proportional to the total number of nuclei) is an important example; each part chosen proportional to the total number of electrons in the system [25]. Thus, $E = E_1 + E_2 + E_3$, where

$$E_1 = -\frac{1}{2} \int d\xi_1 \nabla_1^2 \gamma(\xi_1|\xi'_1) \quad (\text{III.2})$$

is the electronic kinetic energy,

$$E_2 = \frac{1}{2} \sum_{g \neq h} \frac{Z_g Z_h}{R_{gh}} - \sum_{g=1}^M Z_g \int d\xi_1 \frac{\gamma(\xi_1|\xi_1)}{r_{1g}} + \frac{1}{2} \int d\xi_1 d\xi_2 \frac{\gamma(\xi_1|\xi_1) \gamma(\xi_2|\xi_2)}{r_{12}} \quad (\text{III.3})$$

is the sum of the nuclear-nuclear repulsion energy, the electron-nuclear attraction energy, and the electron-electron Coulomb repulsion energy, i.e. the total electrostatic energy, and

$$E_3 = \int d\xi_1 d\xi_2 \frac{\Gamma(\xi_1 \xi_2|\xi_1 \xi_2) - \frac{1}{2} \gamma(\xi_1|\xi_1) \gamma(\xi_2|\xi_2)}{r_{12}} \quad (\text{III.4})$$

is the exchange-correlation energy. In these expressions γ is the first order and Γ the second order reduced density matrix of the electronic system in the state under consideration, Z_g is the charge of nucleus (core) g , and R_{gh} , r_{1g} , and r_{12} are the appropriate interparticle distances.

The electrically neutral system has M nuclei and N electrons so that

$$\sum_{g=1}^M Z_g = N. \quad (\text{III.5})$$

The one matrix is partitioned such that

$$\gamma(\xi_1|\xi'_1) = \sum_{g=1}^M \gamma_g(\xi_1|\xi'_1) \quad (\text{III.6})$$

i.e. each term is associated with one atom (one unit cell). The charge associated with each term is

$$n_g = \int d\xi \gamma_g(\xi|\xi), \quad (\text{III.7})$$

implying that

$$N = \sum_{g=1}^M n_g. \quad (\text{III.8})$$

Each one of the three terms in the electrostatic energy (III.3) contains a long range component, which is such that the three contributions cancel. The first term, the nuclear repulsion energy, is purely long range and will be left as it stands. In order to separate the long and short range contributions to the other two the potential due to the charge distribution γ_g :

$$V_g(\vec{r}_{1g}) = \int d\xi_2 \frac{\gamma_g(\xi_2|\xi_2)}{r_{12}} \quad (\text{III.9})$$

is analyzed. This is a function of \vec{r}_1 . Expanding $1/r_{12}$ in spherical harmonics and rearranging one obtains

$$V_g(\vec{r}_{1g}) = \frac{n_g}{r_{1g}} - \omega(\vec{r}_{1g}), \quad (\text{III.10})$$

where

$$\begin{aligned} \omega(\vec{r}_{1g}) = & \int_{r_{1g}}^{\infty} r_{2g}^2 dr_{2g} \int d\Omega_{2g} \int d\xi_2 \gamma_g(\xi_2|\xi_2) \left[\frac{1}{r_{1g}} - \frac{1}{r_{2g}} \right] \\ & - \sum_{l=1}^{\infty} \int d\xi_2 \gamma_g(\xi_2|\xi_2) \frac{r_{<}^l}{r_{>}^{l+1}} P_l(\cos \vartheta_{12}). \end{aligned} \quad (\text{III.11})$$

Here $r_{<}$ is the smaller and $r_{>}$ the greater of r_{1g} and r_{2g} , respectively, ϑ_{12} the angle between \vec{r}_{1g} and \vec{r}_{2g} , and $d\Omega_{2g}$ the volume element relating to the polar angles of \vec{r}_{2g} .

Use of (III.10) leads to

$$\begin{aligned}
\frac{1}{2} \int d\xi_1 d\xi_2 \frac{\gamma(\xi_1|\xi_1)\gamma(\xi_2|\xi_2)}{r_{12}} &= \frac{1}{2} \sum_{g,h} \int d\xi_1 d\xi_2 \frac{\gamma_g(\xi_1|\xi_1)\gamma_h(\xi_2|\xi_2)}{r_{12}} \\
&= \frac{1}{2} \sum_{g \neq h} \int d\xi_1 \gamma_g(\xi_1|\xi_1) \left[\frac{n_h}{r_{1h}} - \omega(\vec{r}_{1h}) \right] + \frac{1}{2} \sum_g \int d\xi_1 \gamma_g(\xi_1|\xi_1) V_g(\vec{r}_{1g}) \\
&= \frac{1}{2} \sum_{g \neq h} \left[n_h \left(\frac{n_g}{R_{gh}} - \omega(\vec{R}_{gh}) \right) - \int d\xi_1 \gamma_g(\xi_1|\xi_1) \omega(\vec{r}_{1h}) \right] \\
&\quad + \frac{1}{2} \sum_g \int d\xi_1 \gamma_g(\xi_1|\xi_1) V_g(\vec{r}_{1g}).
\end{aligned} \tag{III.12}$$

Similar manipulations of the electron-nuclear attraction term gives

$$\begin{aligned}
-\sum_g Z_g \int d\xi_1 \frac{\gamma(\xi_1|\xi_1)}{r_{1g}} &= -\sum_g Z_g \sum_h \int d\xi_1 \frac{\gamma_h(\xi_1|\xi_1)}{r_{1g}} \\
&= -\sum_{g \neq h} Z_g \left[\frac{n_h}{R_{gh}} - \omega(\vec{R}_{gh}) \right] - \sum_g Z_g \int d\xi_1 \frac{\gamma_g(\xi_1|\xi_1)}{r_{1g}}.
\end{aligned} \tag{III.13}$$

Therefore the long range component of the electrostatic part E_2 of the total energy can be written as

$$\frac{1}{2} \sum_{g \neq h} \frac{(Z_g - n_g)(Z_h - n_h)}{R_{gh}} \tag{III.14}$$

which obviously vanishes when $Z_g = n_g$ for all g .

The short range part of the electrostatic interaction can then be expressed as

$$\begin{aligned}
&\sum_g \int d\xi_1 \gamma_g(\xi_1|\xi_1) \left[\frac{1}{2} V_g(\vec{r}_{1g}) - \frac{Z_g}{r_{1g}} \right] \\
&\quad + \frac{1}{2} \sum_{g \neq h} \left[(2Z_g - n_g) \omega(\vec{R}_{gh}) - \int d\xi_1 \gamma_g(\xi_1|\xi_1) \omega(\vec{r}_{1h}) \right].
\end{aligned} \tag{III.15}$$

Hartree-Fock versus density functional theory

Whenever extended systems are discussed it is unavoidable to touch the question of the basic one-electron approximation. It became clear very early that the Hartree-Fock method is unsuitable for large systems, particularly for metals where it leads to a vanishing density of states at the Fermi energy [26]. This is easily seen for the electron gas and it has been shown much later how this pathology is the result of the conjunction of three factors (i) Coulombic forces, (ii) extended systems, and (iii) the restricted Hartree-Fock method [27, 28]. For nearly thirty years density functional methods [29], based on the Hohenberg-Kohn theorem [30] have provided a better zeroth order description of extended systems, which has led to an unprecedented and

extremely useful interaction between theory and experiment. In the practical implementations of density functional methods the so called "local density approximation" of the exchange-correlation potential still dominates. The weakness of that approximation together with the difficulty of making systematic improvements have during the last few years lead to somewhat of a renaissance of the Hartree-Fock method for extended systems (see for instance volume 42, issue 1 (1992) of the International Journal of Quantum Chemistry). This renewal is coupled with the awareness of the necessity to combine Hartree-Fock with corrections to remedy pathologies as the one alluded to here. In the electron gas case it has been shown explicitly how the Random Phase Approximation (RPA) can provide such corrections [31]. This is sometimes summed up by saying that "Hartree is a better starting point than Hartree-Fock" for extended systems [32].

It should be noted that although the END approach employed here uses a single determinantal wavefunction for the electrons, it is not synonymous with the Hartree-Fock method. The time-dependent END theory at this level of approximation can be labeled as being fully nonlinear Time-Dependent Hartree-Fock (TDHF). The RPA is equivalent to linearized TDHF and thus the present description contains the necessary corrections to the pathologies observed for the Hartree-Fock method.

IV. The model

The purpose of the present paper is to apply the END theory to an extended system. This requires a model that is sufficiently realistic yet not too complicated. A Hamiltonian inspired by the PPP model seems to meet those requirements. For applications to extended systems an important advantage of the PPP model is that it correctly describes the long range aspects of the Coulomb interaction [33].

Originally the PPP method was devised to describe the (optical) π electrons in planar organic molecules. The model employs a basis of atomic p_z orbitals, one on each carbon atom. In order to simplify the calculations one invokes the so called "zero differential overlap" (ZDO) approximation, meaning that in the many-center integrals charge densities associated with atomic orbitals on two different atoms are neglected. This can be considered a reasonable approximation if the atomic orbitals (AO) are interpreted as "orthogonalized atomic orbitals" (OAO) [25, 34]. On the other hand OAO's can be regarded as Wannier functions [25].

As in the PPP model the Hamiltonian is expressed in second quantization and associated with a certain set of basis spin orbitals. For present purposes this basis can be the (exact) solutions to the RHF problem at the equilibrium positions of the nuclei. The canonical solutions are then Bloch functions, whereas the corresponding Wannier functions are certain unitary transformations of these Bloch functions. The corresponding LCAO (linear combination of atomic orbitals) approximation would employ linear combinations of OAO's for the Wannier functions and linear combinations of Bloch sums of the basic AO's for the canonical solutions. In either case one refers to the exact or approximate solutions of the RHF problem at the equilibrium nuclear positions as SCF Bloch functions and SCF Wannier functions. The reasons for this choice of basis are discussed in more detail in section V.

The *SCF Wannier functions* (WF) are expressed as

$$u_{m\sigma}(\xi) = u(\vec{r} - \vec{m})\sigma(\zeta) = u_m(\vec{r})\sigma(\zeta) \quad (\text{IV.1})$$

including a spin factor, and the SCF Bloch functions (BF) become

$$v_{\sigma}(k, \xi) = v(k, \vec{r})\sigma(\zeta) = M^{-1/2} \sum_{m=M/2}^{M/2-1} u_m(\vec{r})e^{ikam}\sigma(\zeta). \quad (\text{IV.2})$$

The inverse transformation ($k = 2\pi\kappa/Ma$) can be expressed as

$$u_m(\vec{r}) = M^{-1/2} \sum_{\kappa=M/2}^{M/2-1} v(k, \vec{r})e^{-ikam}. \quad (\text{IV.3})$$

This means that the wave number k lies in the interval $-\pi/a \leq k < \pi/a$, which is the first Brillouin zone (BZ). The electron field operators $\{a_{\sigma}(m), a_{\sigma}^{\dagger}(m)\}$ correspond to the WF and $\{b_{\sigma}(k), b_{\sigma}^{\dagger}(k)\}$ to the BF, where the subscript refers to the spin. The creation operators transform as the spin orbitals

$$\begin{aligned} b_{\sigma}^{\dagger}(k) &= M^{-1/2} \sum_m^{BK} a_{\sigma}^{\dagger}(m)e^{ikam} \\ a_{\sigma}^{\dagger}(m) &= M^{-1/2} \sum_k^{BZ} b_{\sigma}^{\dagger}(k)e^{-ikam} \end{aligned} \quad (\text{IV.4})$$

and the adjoint relations hold for the annihilation operators.

The Hamiltonian in the WF representation can be expressed as

$$\begin{aligned} H = H_0 &+ \sum_m^{BK} \alpha(m) \sum_{\sigma} n_{\sigma}(m) + \sum_{m \neq n}^{BK} \beta(m, n) a_{\sigma}^{\dagger}(m) a_{\sigma}(n) \\ &+ \frac{1}{2} \sum_{m, n}^{BK} \gamma(m - n) \sum_{\sigma, \sigma'} n_{\sigma}(m) n_{\sigma'}(n) \end{aligned} \quad (\text{IV.5})$$

where the occupation number operator $n_{\sigma}(m) = a_{\sigma}^{\dagger}(m) a_{\sigma}(m)$ and where in the last sum the term with $m = n$ and $\sigma = \sigma'$ is missing.

The diagonal matrix element $\alpha(m)$ of the core Hamiltonian with respect to the Wannier function centered at m is (Q is the atomic core charge)

$$\alpha(m) = \alpha_m - \sum_{n \neq m}^{BK} \frac{Q}{|\vec{R}(m) - \vec{n}|}. \quad (\text{IV.6})$$

The first term depends on the core displacements $\vec{\rho}(m)$ (which are not restricted to any one direction) via a short range potential. The sum can be separated into two terms. A Coulombic one independent of the core displacements that cancels similar terms in the electronic and the nuclear repulsion energies and one that depends on the core displacements. The off-diagonal elements $\beta(m, n)$ of the core Hamiltonian also depend on the displacements via short range

potentials. The parameters $\gamma(n-m)$ represent the interaction between electron density on atom m (or density in cell m) and that on atom n . Due to the choice of basis functions these parameters depend on the distance $|\vec{r}_m - \vec{r}_n| = R$ but not on the displacements. Following Stolarczyk et al. [35] the form

$$\gamma(R) = \frac{1}{R + e^{-\gamma(0)R}/\gamma(0)} = \frac{1}{R} + \lambda(R) \quad (\text{IV.7})$$

is chosen to obtain

$$\lambda^{-1}(R) = -R(1 + \gamma(0)R e^{\gamma(0)R}) \quad (\text{IV.8})$$

which shows that the term $\lambda(R)$ is free of spurious long range effects.

The term H_0 in the Hamiltonian represents the repulsion between cores

$$H_0 = \frac{1}{2} \sum_{m \neq n} \frac{Q^2}{|\vec{R}(m) - \vec{R}(n)|} \quad (\text{IV.9})$$

As discussed in section II the total wavefunction is assumed to be a single Slater determinant. The corresponding one matrix or the Fock-Dirac density matrix in the Wannier representation can be expressed as

$$\gamma(\xi|\xi') = \sum_{m,n} \sum_{\sigma,\sigma'}^{BK} u_{m\sigma}(\xi) D^{\sigma\sigma'}(m,n) u_{n\sigma'}^*(\xi'). \quad (\text{IV.10})$$

The matrix elements $D^{\sigma\sigma'}(m,n)$ clearly depend on the choice of basis and constitute an average over the state under consideration

$$D^{\sigma\sigma'}(m,n) = \langle a_{\sigma'}^\dagger(n) a_{\sigma}(m) \rangle. \quad (\text{IV.11})$$

The notation

$$D^{\alpha\alpha}(m,n) + D^{\beta\beta}(m,n) = D(m,n) \quad (\text{IV.12})$$

is introduced demanding that $D^{\alpha\alpha}(m,m) = D^{\beta\beta}(m,m) = Q/2$ in the reference state, where Q is the core charge of the only type of atom present in the chain.

The average value of the various terms in the Hamiltonian requires the evaluation of the expectation values $\langle n_{\sigma}(m) n_{\sigma'}(n) \rangle$, which for a single determinant becomes [20]

$$\langle n_{\sigma}(m) n_{\sigma'}(n) \rangle = \langle n_{\sigma}(m) \rangle \langle n_{\sigma'}(n) \rangle = D^{\sigma\sigma}(m,m) D^{\sigma'\sigma'}(n,n). \quad (\text{IV.13})$$

The expectation value of the Hamiltonian (IV.5) with respect to a single determinantal state can then be expressed as

$$\begin{aligned} \langle H \rangle = & \frac{Q^2}{2} \sum_{m \neq n}^{BK} \frac{1}{|\vec{R}(m) - \vec{R}(n)|} + \sum_m^{BK} \alpha(m) D(m,m) \\ & + \gamma(0) \sum_m^{BK} D^{\alpha\alpha}(m,m) D^{\beta\beta}(m,m) + \sum_{m \neq n}^{BK} \beta(n,m) D(m,n) \\ & + \frac{1}{2} \sum_{m \neq n}^{BK} \gamma(n-m) \sum_{\nu, \nu'}^{spin} D^{\nu\nu}(m,m) D^{\nu'\nu'}(n,n). \end{aligned} \quad (\text{IV.14})$$

Using the above definitions including (IV.7) and the expansion

$$\frac{1}{|\vec{R} - \vec{r}|} = \frac{1}{R} + \frac{\vec{R} \cdot \vec{r}}{R^3} + \frac{3(\vec{R} \cdot \vec{r})^2 - R^2 r^2}{2R^5} + \dots \quad (\text{IV.15})$$

for $r \ll R$, the monopole terms are

$$\frac{1}{2a} \sum_{m \neq n}^{BK} \frac{[Q - D(m, m)][Q - D(n, n)]}{|m - n|}. \quad (\text{IV.16})$$

This expression corresponds to (III.14) in the general treatment. For ionic systems this is the Madelung energy. It vanishes when $Q = D(m, m)$ for all m , a condition that means that the number of electrons associated with atom m is the same as the core charge. This is the case for the reference state. When the nuclei vibrate and the electrons react to this motion the atomic charges will fluctuate. The fluctuations around the equilibrium charge add up to zero, while expression (IV.16) represents the Madelung energy of these fluctuating atomic charges. It follows that the requirement

$$\sum_m^{BK} D(m, m) = MQ \quad (\text{IV.17})$$

is a reasonable one.

In sections VII and VIII a particular kind of fluctuations are introduced such that

$$D(m, m) = Q + (-)^m q, \quad (\text{IV.18})$$

which obviously satisfies condition (IV.17), and gives the Madelung energy

$$\frac{q^2}{2a} \sum_{m \neq n}^{BK} \frac{(-1)^{m-n}}{|m - n|} = -\frac{Mq^2 \ln 2}{a}. \quad (\text{IV.19})$$

This condition is assumed to hold in the following analysis.

The next set of terms in the multipole expansion (IV.15) are

$$\frac{Q}{a^2} \sum_{m \neq n}^{BK} \frac{(m - n) \rho_x(m)}{|m - n|^3} [Q - D(m, m)], \quad (\text{IV.20})$$

an expression that also vanishes under the condition $Q = D(m, m)$ for all m , and also with the special choice (IV.18) this sum is zero, since

$$\begin{aligned} & -\frac{Qq}{a^2} \sum_{m \neq n}^{BK} \frac{(-1)^m (m - n)}{|m - n|^3} \rho_x(m) \\ &= \frac{Qq}{a^2} \sum_m^{BK} (-1)^m \rho_x(m) \sum_{n \neq 0}^{BK} \frac{n}{|n|^3} = 0. \end{aligned} \quad (\text{IV.21})$$

However, a state with general fluctuating charges will contribute to the Madelung energy. Similarly, some of the terms proportional to a^{-3} vanish, so that for small vibrations

$$\begin{aligned}
\langle H \rangle = & \frac{Q^2}{2a^3} \sum_{m \neq n}^{BK} \frac{\rho_x(m)\rho_x(n) + \rho_y(m)\rho_y(n) - 2\rho_z(m)\rho_z(n)}{|\vec{m} - \vec{n}|^3} \\
& + Q \sum_m^{BK} \alpha_m - \frac{Mq^2 \ln 2}{a} \\
& + \gamma(0) \sum_m^{BK} D^{\alpha\alpha}(m, m) D^{\beta\beta}(m, m) + \sum_{n \neq m}^{BK} \beta(n, m) D(m, n) \\
& + \frac{1}{2} \sum_{m \neq n}^{BK} \lambda(n - m) D(m, m) D(n, n).
\end{aligned} \tag{IV.22}$$

In somewhat more detail than expressed by (IV.18) one finds

$$D_{\pm}(m, m) = \frac{Q}{2} + (-1)^m q_{\pm} \tag{IV.23}$$

where the notations $D^{\alpha\alpha} \equiv D_+$ and $D^{\beta\beta} \equiv D_-$ have been introduced. One may then also write

$$\sum_m^{BK} D_+(m, m) D_-(m, m) = M \left[\frac{Q^2}{4} + q_+ q_- \right]. \tag{IV.24}$$

The parameters α_m and $\beta(m, n)$ are due to the short range forces within and between the cores and are expanded in terms of the displacements as

$$Q\alpha_m = Q\alpha^0 + \sum_j^{x,y,z} A_j \rho_j(m) + \frac{1}{2} \sum_{j,j'}^{x,y,z} A_{jj'} \rho_j(m) \rho_{j'}(m), \tag{IV.25}$$

and

$$\begin{aligned}
\beta(n, m) = & \beta^0(n, m) + \sum_j^{x,y,z} \beta_j^0(n, m) [\rho_j(n) - \rho_j(m)] \\
& + \frac{1}{2} \sum_{j,j'}^{x,y,z} \beta_{jj'}^0(n, m) \rho_j(n) \rho_{j'}(m).
\end{aligned} \tag{IV.26}$$

This result has been obtained using the relation $\beta_j^0(n, m) = -\beta_j^0(m, n)$ for the first derivatives. The total energy separates into two parts, one, E_d consisting of those terms that depend on the nuclear displacements and another, E_{st} being the energy of the system with the static lattice, i.e.

$$\langle H \rangle = E_{st} + E_d \tag{IV.27}$$

with

$$E_{st} = M \{ Q\alpha^0 + \sum_{n \neq m}^{BK} \beta^0(n, m) D(m, n) + \gamma(0) [\frac{Q^2}{4} + q_+ q_-] + \frac{Q^2}{2} \sum_{m \neq 0}^{BK} \lambda(m) + \frac{q^2}{2} [\sum_{n \neq 0} (-1)^n \lambda(n) - \frac{\ln 2}{a}] \}, \quad (IV.28)$$

and

$$E_d = \frac{Qq}{2a^3} \sum_{m \neq n}^{BK} \frac{(-1)^m}{|m-n|^3} [\rho_x^2(m) + \rho_y^2(m) + \rho_z^2(m)] + \frac{Q^2}{2a^3} \sum_{m \neq n}^{BK} \frac{\rho_x(m)\rho_x(n) + \rho_y(m)\rho_y(n) - 2\rho_z(m)\rho_z(n)}{|m-n|^3} + \sum_m^{BK} \sum_j^{z,y,z} A_j \rho_j(m) + \frac{1}{2} \sum_m^{BK} \sum_{j,j'}^{z,y,z} A_{jj'} \rho_j(m) \rho_{j'}(m) + \sum_{m \neq n}^{BK} [D(n, m) + D(m, n)] \{ \sum_j^{z,y,z} \beta_j^0(n, m) \rho_j(n) + \frac{1}{4} \sum_{j,j'}^{z,y,z} \beta_{jj'}^0(n, m) \rho_j(n) \rho_{j'}(m) \}. \quad (IV.29)$$

The first and the last term in the expression for E_d are really of higher order and are not part of the harmonic approximation, but kept here to show how such terms enter. The nuclear displacements and the dynamical variables z can be chosen such that they are zero at a stationary point, which means that

$$\left. \frac{\partial(E_{st} + E_d)}{\partial z} \right|_{z=0} = \left. \frac{\partial(E_{st} + E_d)}{\partial \rho} \right|_{z=0} = 0 \quad (IV.30)$$

are the equations defining the stationary point. The symmetrized factor $[D(m, n) + D(n, m)]$ guarantees a real result for the last term.

V. Electronic basis functions

The choice of basis functions for the description of electrons in a system with moving nuclei requires careful analysis. Only the situation where the nuclei undergo small vibrations always keeping them close to their equilibrium positions is considered. In principle, a complete set of electronic basis functions is needed. Formally such a set is available in the form of all the solutions of the band theory problem for the equilibrium positions of the nuclei. Such a basis is obtained as the solutions to an effective one-electron equation for a static, fully periodic lattice. At this stage of the discussion there is no need to specify that equation in more detail. It could be, say, of Hartree-Fock type, of density functional type, or something else. What is needed is the property common to all such equations, namely the translational symmetry, which implies that the solutions are Bloch functions, i.e. eigenfunctions of the translation operator.

In actual calculations a specific choice of such Bloch functions obviously has to be made. The calculation of the energy bands and the corresponding wavefunctions is a well developed procedure [36, 37] and there are a number of possible choices for representing the solutions to the static lattice problem in terms of specific basis functions. This presentation limits the discussion to the case when the original basis functions are atomic orbitals of some kind centered at the equilibrium nuclear positions. From each type of atomic orbital in a unit cell a Bloch sum can be formed adapted to the translational symmetry. The final solutions of the effective one-electron problem are then linear combinations of such Bloch sums. The term 'SCF Bloch functions' are used for such solutions.

Given any set of Bloch functions in a band the corresponding set of Wannier functions can always be constructed by means of a unitary transformation [38]. If that is done with a set of Bloch functions expressed as linear combinations of Bloch sums of atomic orbitals, the resulting Wannier functions can be closely approximated by linear combinations of orthogonalized atomic orbitals. But the unitary transformation can also be carried out on the exact solutions to the static lattice problem, and that may be valuable from a formal point of view. The formally exact Wannier functions are then obtained, which constitute a set of non-canonical orbitals for the single determinantal wavefunction to represent the solution of the static lattice problem.

The functions (IV.1) and (IV.2) primarily represent such exact canonical and non-canonical solutions of the effective one-electron static lattice problem. They do not constitute a complete set of functions since they correspond to only one band. But, in principle, it is possible to include more than one band. These functions provide a good description of the system at the equilibrium nuclear positions. For small departures from the equilibrium positions it would therefore seem natural to employ these functions as a basis for the END treatment. Since the term "basis function" is used in several different contexts one should clarify the following points. The electronic basis functions for the END treatment are the exact or approximate solutions of the effective one-electron equation for the static lattice problem, i.e. functions (IV.1) and (IV.2). The parameters characterizing the PPP Hamiltonian are thus expressed in terms of these functions.

In *ab initio* calculations obviously more specific choices have to be made. One can discern two distinct alternatives. One would be to use the primitive basis of Gaussians centered at the nuclei. These basis functions are allowed to follow the nuclear motion. At any given moment the nuclear framework shows no particular symmetry. This approach has led to successful descriptions of small molecular systems. However, for an extended system the lack of periodicity means that one cannot speak about Bloch or Wannier functions, leading to great complications. The other possibility, which has been chosen here, is based on the notion that the nuclei never depart very far from the regular equilibrium positions and the SCF Bloch or Wannier functions will be adequate choices.

Using the Bloch or Wannier functions in one band means that the possibility for the electrons to adjust to the changing nuclear environment resides in mixing the spin orbitals used in the reference determinant with, in principle, all virtual spin orbitals. In order to explore the effects of such mixing in a somewhat systematic fashion the pairing of each reference spin orbital with one virtual spin orbital is first considered. This can be looked upon as a successive lowering of the translational symmetry. Since the translational symmetry can also be used to classify normal modes of vibration, such pairings should provide a number of useful special cases of END.

VI. Lattice dynamics

In order to connect the END treatment of vibrational and electronic structure with more traditional procedures this section treats the special case where the total energy in the equations of motion (II.6) does not depend on the electronic dynamic variables.

With only nuclear dynamic variables the equations of motion reduce to

$$\begin{aligned} -dP/dt &= \partial E / \partial R \\ dR/dt &= \partial E / \partial P \end{aligned} \quad (VI.1)$$

i.e. the classical Hamilton's equations of motion.

Restricting the considerations to longitudinal vibrations, i.e. dynamics for which $\rho_x(m) = \rho_y(m) = 0$ for all m leads to simpler and more transparent expressions than those of the full treatment while clearly displaying the capabilities of the model. Adding the nuclear kinetic energy to (IV.27), and using (IV.30) yields

$$\begin{aligned} E &= E_{st} + E_d + \sum_m^{BK} \frac{P_z^2}{2M_n} \\ &= E_{st} - \frac{1}{a^3} \sum_{m \neq n}^{BK} \frac{\rho_x(m)\rho_x(n)}{|\vec{r}_m - \vec{r}_n|^3} + \frac{1}{2} \sum_m^{BK} A_{zz} \rho_x^2(m) \\ &\quad + \frac{1}{2} \sum_{m \neq n}^{BK} B_{zz}(n, m) \rho_x(m)\rho_x(n) + \sum_m^{BK} \frac{P_z^2(m)}{2M_n}. \end{aligned} \quad (VI.2)$$

The core charge is set to $Q = 1$ and the following notation is introduced

$$B_{jj'}(n, m) = D_0(n, m) \beta_{jj'}^0(n, m), \quad (VI.3)$$

with $[j, j' = x, y, \text{ or } z]$ It should be noted that the density matrix of the reference state satisfies the relation $D_0(n, m) = D_0(n - m, 0)$. In equation (VI.3) and in the expression for E_{st} the density matrix D_0 of the reference state appears. The energy derivatives with respect to displacements then are

$$\frac{\partial E}{\partial \rho_x(m)} = -\frac{2}{a^3} \sum_{n \neq m}^{BK} \frac{\rho_x(n)}{|\vec{r}_m - \vec{r}_n|^3} + A_{zz} \rho_x(m) + \sum_{n \neq m}^{BK} B_{zz}(m, n) \rho_x(n). \quad (VI.4)$$

Thus, the coupling between different nuclear displacements is due to the "hopping parameters" β in the Hamiltonian and also introduced via the multipole expansion.

The equations of motion for this special case (longitudinal nuclear motion and one kind of nuclei with mass M_n)

$$\begin{aligned} -\frac{dP_x(m)}{dt} &= \frac{\partial E}{\partial \rho_x(m)} \\ \frac{d\rho_x(m)}{dt} &= \frac{\partial E}{\partial P_x(m)} \end{aligned} \quad (VI.5)$$

can be combined into

$$M_n \frac{d^2 \rho_z(m)}{dt^2} = - \frac{\partial E}{\partial \rho_z(m)}. \quad (\text{VL6})$$

Expanding the displacements in normal coordinates $Q(q, t)$, such that

$$\rho_z(m) = \frac{1}{\sqrt{MM_n}} \sum_q^{BZ} Q(q, t) e^{iqam}, \quad (\text{VL7})$$

substituting this into the equation of motion, multiplying by $\exp(-iqam)$, and summing over m yield

$$M_n \frac{d^2 Q(q, t)}{dt^2} = \left\{ \frac{2}{a^3} \sum_{n \neq 0}^{BK} \frac{e^{-iqan}}{|n|^3} - A_{zz} - \sum_{n \neq 0}^{BK} B_{zz}(n, 0) e^{iqan} \right\} Q(q, t). \quad (\text{VL8})$$

The ansatz

$$Q(q, t) = Q_0(q) e^{-i\omega(q)t} \quad (\text{VL9})$$

used in equation (VL8) yields the following expression for the longitudinal frequency

$$\begin{aligned} \omega^2(q) &= \frac{1}{M_n} \left\{ -\frac{2}{a^3} \sum_{n \neq 0}^{BK} \frac{e^{-iqan}}{|n|^3} + A_{zz} + \sum_{n \neq 0}^{BK} B_{zz}(n, 0) e^{-iqan} \right\} \\ &= \frac{1}{M_n} \left\{ -\frac{4}{a^3} \sum_{n=1}^{M/2-1} \frac{\cos(qan)}{n^3} + A_{zz} + 2 \sum_{n=1}^{M/2-1} B_{zz}(n, 0) \cos(qan) \right\}. \end{aligned} \quad (\text{VL10})$$

In order to get the correct behavior for small q , i.e. $\omega(q) \rightarrow 0$ the condition

$$-\frac{4}{a^3} \sum_{n=1}^{M/2-1} \frac{1}{n^3} + A_{zz} + 2 \sum_{n=1}^{M/2-1} B_{zz}(n, 0) = 0 \quad (\text{VL11})$$

is needed.

The inverse transformation

$$Q(q, t) = \sqrt{\frac{M_n}{M}} \sum_m^{BK} \rho_z(m) e^{-iqam}, \quad (\text{VL12})$$

of the displacements together with the condition that $\rho_z(m)$ are real, gives the relation $Q^*(q, t) = Q(-q, t)$. The general expression for the displacements can then be written as

$$\rho_z(m) = \frac{1}{\sqrt{MM_n}} \left\{ Q_0 + \sum_{q>0}^{BZ} [Q_1(q, t) \cos qam - Q_2(q, t) \sin qam] \right\}, \quad (\text{VL13})$$

with the real and imaginary parts of the normal coordinates given by

$$\begin{aligned} Q_1(q, t) &= Q_{01}(q) \cos \omega_l(q)t + Q_{02}(q) \sin \omega_l(q)t \\ Q_2(q, t) &= -Q_{01}(q) \sin \omega_l(q)t + Q_{02}(q) \cos \omega_l(q)t. \end{aligned} \quad (\text{VI.14})$$

Should transversal vibrations also be included in (VI.2) the general expression becomes

$$\begin{aligned} E = E_{st} &+ \frac{1}{2a^3} \sum_{n \neq m}^{BK} \frac{\rho_x(m)\rho_x(n) + \rho_y(m)\rho_y(n) - 2\rho_z(m)\rho_z(n)}{|m-n|^3} + \\ &+ \frac{1}{2} \sum_m^{BK} \sum_{j,j'}^{z,y,z} A_{jj'} \rho_j(m) \rho_{j'}(m) \\ &+ \frac{1}{2} \sum_{n \neq m}^{BK} \sum_{j,j'}^{z,y,z} B_{jj'}(n, m) \rho_j(m) \rho_{j'}(n) + \sum_m^{BK} \frac{\tilde{\beta}^2}{2M_n}. \end{aligned} \quad (\text{VI.15})$$

Thus, the one-center parameters induce couplings between different nuclear displacement components on the same atom, while the "hopping parameters" β produce the couplings between all components on different atoms.

VII. Time-dependent band theory

As another special case the END equations for fixed nuclei are studied. This is the Born-Oppenheimer starting point for most problems of electronic structure. The equations of motion (II.6) that determine the time evolution of the electronic state now reduce to

$$\begin{pmatrix} iC & 0 \\ 0 & -iC^* \end{pmatrix} \begin{pmatrix} dz/dt \\ dz^*/dt \end{pmatrix} = \begin{pmatrix} \partial E / \partial z^* \\ \partial E / \partial z \end{pmatrix}. \quad (\text{VII.1})$$

The electronic basis consists of all the SCF Bloch (IV.2) or SCF Wannier (IV.1) functions in a particular band. The most general combination of spin orbitals is of the form

$$v_\sigma(k, \xi) + \sum_{k', \sigma'}^{RZ} v_{\sigma'}(k', \xi) z_{k'\sigma'; k\sigma}(t); \quad (k \text{ in LZ}). \quad (\text{VII.2})$$

Here the abbreviation LZ = Little Zone is used for the interval $-\pi/2a \leq k < \pi/2a$ and RZ = Residual Zone for the remainder of the first Brillouin Zone (BZ), which consists of the two intervals $-\pi/a \leq k < -\pi/2a$ and $\pi/2a \leq k < \pi/a$. The reference determinant is doubly filled with the orbitals $v(k, \vec{r})$ in the LZ. The virtual orbitals $v(k', \vec{r})$ are characterized by the wave numbers k' in RZ.

The possibility of using fully general spin orbitals like (VII.2) should certainly be considered. Here the case where each spin orbital has either α or β spin is first explored. The corresponding orbitals are then in general different. One set of orbitals $w_+(k, \vec{r})$ is combined with α and another set $w_-(k, \vec{r})$ with β spin,

$$\begin{aligned} w_+(k, \vec{r}) &= v(k, \vec{r}) + \sum_{k'}^{RZ} v(k', \vec{r}) z_{+, k'k}(t); \quad (k \text{ in LZ}) \\ w_-(k, \vec{r}) &= v(k, \vec{r}) + \sum_{k'}^{RZ} v(k', \vec{r}) z_{-, k'k}(t); \quad (k \text{ in LZ}). \end{aligned} \quad (\text{VII.3})$$

Each set of these functions can without loss of generality be chosen orthogonal, even though they are not normalized to unity, *i.e.*

$$\int w_{\pm}^*(k, \vec{r}) w_{\pm}(l, \vec{r}) d\vec{r} = d_{\pm k l} \quad (\text{VII.4})$$

$$d_{\pm k} = 1 + \sum_{k'}^{RZ} z_{\pm; k' k}^* z_{\pm; k' k} = 1 + \left(z_{\pm}^{\dagger} z_{\pm} \right)_{kk}.$$

Because of the pairing theorem [39] the z parameters can be assumed to satisfy

$$\int w_{\pm}^*(k, \vec{r}) w_{\mp}(l, \vec{r}) d\vec{r} = \lambda_{\pm k l} \quad (\text{VII.5})$$

$$\lambda_{\pm k} = 1 + \left(z_{\pm}^{\dagger} z_{\mp} \right)_{kk}.$$

Thus, both the two $(M/2) \times (M/2)$ matrices d_{\pm} and λ_{\pm} and the product matrices $z_{+}^{\dagger} z_{-}$ and $z_{-}^{\dagger} z_{+}$ are diagonal.

The corresponding Fock-Dirac density matrix

$$\rho(\xi, \xi') = \rho_{+}(\vec{r}, \vec{r}') \alpha(\zeta) \alpha(\zeta') + \rho_{-}(\vec{r}, \vec{r}') \beta(\zeta) \beta(\zeta')$$

$$\rho_{\pm}(\vec{r}, \vec{r}') = \sum_k^{LZ} d_{\pm k}^{-1} w_{\pm}(k, \vec{r}) w_{\pm}^*(k, \vec{r}'). \quad (\text{VII.6})$$

can then be expressed in terms of the z 's (see *e.g.* [8]). The basic Bloch functions are here assumed to be solutions of a restricted Hartree-Fock problem and time reversal symmetry would imply that

$$v(-k, \vec{r}) = v^*(k, \vec{r}) \quad (\text{VII.7})$$

$$v(-k', \vec{r}) = v^*(k', \vec{r}).$$

There is no reason to impose such relations on the functions (VII.3).

In order to illustrate how the END method works the case with only two z -parameters per wave number in LZ is studied, so that

$$w_{+}(k, \vec{r}) = v(k, \vec{r}) + z_{+; k' k} v(k', \vec{r}) \quad (\text{VII.8})$$

$$w_{-}(k, \vec{r}) = v(k, \vec{r}) + z_{-; k' k} v(k', \vec{r}).$$

This is an example of *pairing* which can be made in several different ways, both with respect to the spatial orbitals and with respect to spin [40]. A determinant with half of the electrons filling w_{+} orbitals with spin α , and the other half filling w_{-} orbitals with spin β forms the basis for the Alternant Molecular Orbital (AMO) method (see [41] and references therein). In applications of the AMO method to the description of solids [42] the pairing is chosen such that

$$k' = k + \pi/a; \quad k \text{ in LZ}; \quad k' \text{ in RZ}. \quad (\text{VII.9})$$

One could, of course, leave k' unspecified within RZ in developing the formal theory, and a variety of choices could be explored in actual applications. In order to demonstrate the principles

of the END theory it suffices to limit the present development to the choice in equation (VII.9), and write

$$z_{\pm; k'k} = z_{\pm k}. \quad (\text{VII.10})$$

This means that there are $M/2$ dynamical variables $z_{+k}(t)$ for electrons with up-spin and an equal number of variables $z_{-k}(t)$ for down-spin electrons. The density matrix coefficients (i.e. elements of the so called charge and bond order matrix) are then

$$D_{\pm}(m, n) = \frac{1}{M} \sum_k^{LZ} e^{ikn(m-n)} \{1 + (-1)^n z_{\pm k}^* + (-1)^m z_{\pm k} + [(-1)^{m-n} - 1] |z_{\pm k}|^2 + \dots\}, \quad (\text{VII.11})$$

such that

$$D(m, n) = D_+(m, n) + D_-(m, n) = D_0(m, n) + D_1(m, n) + D_2(m, n) \quad (\text{VII.12})$$

in terms of the zeroth, first and second order terms (terminating after second order) in the electronic dynamical variables. This gives

$$\begin{aligned} & \sum_{m \neq n}^{BK} \beta^0(m, n) D(m, n) \\ &= M \left\{ B - \frac{2}{M} \sum_{m=\text{odd}}^{BK} \beta^0(m, 0) \sum_k^{LZ} [|z_{+k}|^2 + |z_{-k}|^2] e^{ikm} \right\}, \end{aligned} \quad (\text{VII.13})$$

with

$$B = -\frac{4}{\pi} \sum_{m=\text{odd} > 0}^{BK} \frac{(-1)^{(3m-1)/2}}{m} \beta^0(m, 0). \quad (\text{VII.14})$$

For the diagonal elements in (VII.11)

$$D_{\pm}(m, m) = \frac{1}{2} + \frac{(-1)^m}{M} \sum_k^{LZ} \{z_{\pm k}^* + z_{\pm k}\} = \frac{1}{2} + (-1)^m q_{\pm} \quad (\text{VII.15})$$

Adding the contributions from the two spins yields

$$D(m, m) = D_+(m, m) + D_-(m, m) = 1 + (-1)^m q \quad (\text{VII.16})$$

with $q = q_+ + q_-$ and with $(-1)^m q(t)$ representing the fluctuating charge at site m , such that

$$\sum_m^{BK} (-1)^m q(t) = 0 \quad (\text{VII.17})$$

at all times. An equation for the total static energy form (IV.28) can then be obtained as

$$\begin{aligned}
E_{st} = & M \left\{ q^2 \left[-\frac{\ln 2}{a} + \frac{1}{2} \sum_{n \neq 0}^{BK} (-1)^n \lambda(n) \right] + \alpha^0 \right. \\
& + B + \gamma(0) \left[\frac{1}{4} + q_+ q_- \right] + \frac{1}{2} \sum_{n \neq 0}^{BK} \lambda(n) \} \\
& - 2 \sum_{m=\text{odd}}^{BK} \beta^0(m, 0) \sum_k^{LZ} [|z_{+k}|^2 + |z_{-k}|^2] e^{ikam}.
\end{aligned} \tag{VII.18}$$

Differentiation with respect to the z variables gives

$$\begin{aligned}
\frac{\partial E_{st}}{\partial z_{+k}} &= 2A_0 q + \gamma(0) q_- - 2B(k) z_{+k}^* \\
\frac{\partial E_{st}}{\partial z_{-k}} &= 2A_0 q + \gamma(0) q_+ - 2B(k) z_{-k}^*
\end{aligned} \tag{VII.19}$$

and their complex conjugates, where,

$$A_0 = -\frac{\ln 2}{a} + \frac{1}{2} \sum_{n \neq 0}^{BK} (-1)^n \lambda(n) \tag{VII.20}$$

and

$$B(k) = \sum_{m=\text{odd}}^{BK} \beta^0(m, 0) e^{ikam}. \tag{VII.21}$$

For k in LZ it holds that $B(k) < 0$. It follows from (VII.19) that the derivatives vanish when the z variables do, i.e. the electronic dynamical variables are defined relative to a stationary point of E_{st} .

The dynamical metric is obtained from

$$S = \langle \mathbf{z} | \mathbf{z} \rangle = \prod_{k \in LZ} \{ (1 + |z_{+k}|^2)(1 + |z_{-k}|^2) \}, \tag{VII.22}$$

giving

$$\begin{aligned}
C_{+k, +l} &= \frac{\partial^2 \ln S}{\partial z_{+k}^* \partial z_{+l}} = \delta_{kl} / (1 + |z_{+k}|^2)^2, \\
C_{-k, -l} &= \frac{\partial^2 \ln S}{\partial z_{-k}^* \partial z_{-l}} = \delta_{kl} / (1 + |z_{-k}|^2)^2, \\
C_{+k, -l} &= C_{-k, +l} = 0.
\end{aligned} \tag{VII.23}$$

For the harmonic approximation the dynamical metric is needed only through zeroth order, i.e.

$$C_{+k, +l} = C_{-k, -l} = \delta_{kl} \tag{VII.24}$$

yielding the equations of motion

$$\begin{aligned} i \frac{dz_{+k}}{dt} &= 2A_0 q + \gamma(0)q_- - 2B(k)z_{+k} \\ i \frac{dz_{-k}}{dt} &= 2A_0 q + \gamma(0)q_+ - 2B(k)z_{-k} \end{aligned} \quad (\text{VII.25})$$

and their complex conjugates. Introducing the variables $u_k = z_{+k} - z_{-k}$, leads to

$$i \frac{du_k}{dt} = -\frac{\gamma(0)}{M} \sum_l^{LZ} (u_l + u_l^*) - 2B(k)u_k \quad (\text{VII.26})$$

and its complex conjugate. In matrix form

$$\begin{bmatrix} i1 & 0 \\ 0 & -i1 \end{bmatrix} \begin{bmatrix} \dot{u} \\ \dot{u}^* \end{bmatrix} = \begin{bmatrix} A_1 - 2B & A_1 \\ A_1 & A_1 - 2B \end{bmatrix} \begin{bmatrix} u \\ u^* \end{bmatrix} \quad (\text{VII.27})$$

with

$$u = \begin{bmatrix} \vdots \\ u_k \\ \vdots \end{bmatrix} \quad (\text{VII.28})$$

a column matrix containing the $M/2$ variables u_k , the $(M/2) \times (M/2)$ matrix

$$A_1 = -\frac{\gamma(0)}{M} \begin{bmatrix} 1 & 1 & \cdots & 1 \\ 1 & 1 & \cdots & 1 \\ \vdots & \vdots & \cdots & \vdots \\ 1 & 1 & \cdots & 1 \end{bmatrix}, \quad (\text{VII.29})$$

and the diagonal matrix

$$B = \begin{bmatrix} B(k_{-M/4}) & 0 & \cdots & 0 \\ 0 & B(k_{-M/4+1}) & \cdots & 0 \\ \vdots & \vdots & \cdots & \vdots \\ 0 & 0 & \cdots & B(k_{M/4+1}) \end{bmatrix}. \quad (\text{VII.30})$$

The solution of the dynamical equations can be accomplished by the *ansatz*

$$\begin{bmatrix} u \\ u^* \end{bmatrix} = \begin{bmatrix} X & 1 \\ 1 & X \end{bmatrix} \begin{bmatrix} e^{i\Omega t} & 0 \\ 0 & e^{-i\Omega t} \end{bmatrix} \begin{bmatrix} v \\ v^* \end{bmatrix}, \quad (\text{VII.31})$$

where the time dependence is confined to the matrix blocks $e^{\pm i\Omega t}$, which are diagonal with elements $\exp[\pm i\omega_1(k)t]$. Substituting (VII.31) in (VII.27) and writing

$$V = e^{i\Omega t} v; \quad V^* = e^{-i\Omega t} v^*, \quad (\text{VII.32})$$

lead to a set of homogeneous linear equations

$$\begin{bmatrix} a & b \\ b & a \end{bmatrix} \begin{bmatrix} V \\ V^* \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix}, \quad (\text{VII.33})$$

with

$$\begin{aligned} \mathbf{a} &= -\mathbf{X}\Omega - (\mathbf{A}_1 - 2\mathbf{B})\mathbf{X} - \mathbf{A}_1 \\ \mathbf{b} &= \Omega - (\mathbf{A}_1 - 2\mathbf{B}) - \mathbf{A}_1\mathbf{X}. \end{aligned} \quad (\text{VII.34})$$

Partitioning of (VII.33) yields

$$[\mathbf{a} - \mathbf{b}\mathbf{a}^{-1}\mathbf{b}]\mathbf{V} = 0 \quad (\text{VII.35})$$

and the frequencies $\omega_1(k)$ are obtained from the secular equation

$$\det\{\mathbf{a} - \mathbf{b}\mathbf{a}^{-1}\mathbf{b}\} = 0. \quad (\text{VII.36})$$

The dynamical variables can then be expressed as

$$u_k(t) = v_k^* e^{-i\omega_1(k)t} + \sum_l^{LZ} X_{kl} v_l e^{i\omega_1(l)t}. \quad (\text{VII.37})$$

Equation (VII.25) yields a completely analogous treatment for $g_k = z_{+k} + z_{-k}$ as that just completed for u_k . One gets

$$g_k(t) = w_k^* e^{-i\omega_2(k)t} + \sum_l^{LZ} Y_{kl} w_l e^{i\omega_2(l)t}. \quad (\text{VII.38})$$

The original dynamical parameters are obtained as

$$\begin{aligned} z_{+k} &= \frac{1}{2}(g_k + u_k) \\ z_{-k} &= \frac{1}{2}(g_k - u_k). \end{aligned} \quad (\text{VII.39})$$

VIII. Combined electronic-nuclear dynamics

This section presents a simple case where both electronic and nuclear dynamical variables are allowed to vary simultaneously. The starting point is the harmonic approximation of the energy for longitudinal vibrations and for paired dynamical spin orbitals as discussed in the previous section. The core charge is set to unity ($Q = 1$), and the total energy of the system is

$$E = E_{st} + E_d + T_n \quad (\text{VIII.1})$$

with

$$\begin{aligned} E_{st} &= M \left\{ q^2 \left[-\frac{\ln 2}{a} + \frac{1}{2} \sum_{n \neq 0}^{BK} (-1)^n \lambda(n) \right] + \alpha^0 \right. \\ &\quad \left. + B + \gamma(0) \left[\frac{1}{4} + q_+ q_- \right] + \frac{1}{2} \sum_{n \neq 0}^{BK} \lambda(n) \right\} \\ &\quad - 2 \sum_{m=\text{odd}}^{BK} \beta^0(m, 0) \sum_k^{LZ} [|z_{+k}|^2 + |z_{-k}|^2] e^{ikam}. \end{aligned} \quad (\text{VIII.2})$$

$$\begin{aligned}
E_d = & -\frac{q}{a^3} \sum_{m \neq n}^{BK} \frac{(-1)^m \rho_z^2(m)}{|m-n|^3} - \frac{1}{a^3} \sum_{m \neq n}^{BK} \frac{\rho_z(m) \rho_z(n)}{|m-n|^3} \\
& + \sum_m^{BK} A_z \rho_z(m) + \frac{1}{2} \sum_m^{BK} A_{zz} \rho_z^2(m) \\
& + \sum_{m \neq n}^{BK} \{ [D(m, n) + D(n, m)] [\beta_z^0(m, n) \rho_z(m) + \frac{1}{4} \beta_{zz}^0(m, n) \rho_z(m) \rho_z(n)] \},
\end{aligned} \tag{VIII.3}$$

and

$$T_n = \sum_m^{BK} \frac{P_z^2(m)}{2M_n}. \tag{VIII.4}$$

The density matrix $D_{\pm}(m, n)$ contains terms of zeroth, first, and second order in the electronic dynamical variables [cf (VII.11)],

$$D_{\pm}(m, n) = D_0(m, n) + D_{\pm,1}(m, n) + D_{\pm,2}(m, n). \tag{VIII.5}$$

Since $q = q_+ + q_-$ is of first order in the electronic coordinates the first term in (VIII.3) is really of third order overall and should not enter in the harmonic approximation. This term is neglected as well as other terms of higher order than two in the dynamical variables. Differentiation with respect to the nuclear displacements yields the following expression

$$\begin{aligned}
\frac{\partial E}{\partial \rho_z(m)} = & -\frac{2}{a^3} \sum_{n \neq m}^{BK} \frac{\rho_z(n)}{|n-m|^3} + A_z + A_{zz} \rho_z(m) \\
& + \sum_{n \neq m}^{BK} [D_0(m, n) + D_1(m, n) + D_0(n, m) + D_1(n, m)] \beta_z^0(m, n) \\
& + \sum_{n \neq m}^{BK} D_0(m, n) \beta_{zz}^0(m, n) \rho_z(n).
\end{aligned} \tag{VIII.6}$$

Assuming, as is done here, that the reference state corresponds to a stationary point of the energy implies that

$$\left. \frac{\partial E}{\partial \rho_z(m)} \right|_{\rho=z=0} = A_z + 2 \sum_{n \neq m}^{BK} D_0(m, n) \beta_z^0(m, n) = 0 \tag{VIII.7}$$

for all m . The only term in (VIII.6) which contains the electronic dynamical variables is

$$\begin{aligned}
& \sum_{n \neq m}^{BK} [D_1(m, n) + D_1(n, m)] \beta_z^0(m, n) = \\
& \frac{2(-1)^m}{M} \sum_k^{LZ} \{ \beta(k)(z_{+k} + z_{-k}) \\
& \quad + \beta^*(k)(z_{+k}^* + z_{-k}^*) \},
\end{aligned} \tag{VIII.8}$$

where

$$\begin{aligned}\beta(k) &= \beta_c(k) + i\beta_s(k), \\ \beta_c(k) &= \sum_{n=\text{even}} \beta_s^0(n, 0) \cos(kan), \\ \beta_s(k) &= \sum_{n=\text{odd}} \beta_s^0(n, 0) \sin(kan).\end{aligned}\tag{VIII.9}$$

Since the derivatives $\beta_s^0(n, 0)$ are odd functions of n $\beta_c(k) = 0$. Using (VII.19) and (VIII.1) the derivatives with respect to the z variables become

$$\begin{aligned}\frac{\partial E}{\partial z_{+k}} &= 2A_0q + \gamma(0)q_- - 2B(k)z_{+k}^* + 2\beta(k)\frac{1}{M} \sum_m^{BK} (-1)^m \rho_z(m), \\ \frac{\partial E}{\partial z_{-k}} &= 2A_0q + \gamma(0)q_+ - 2B(k)z_{-k}^* + 2\beta(k)\frac{1}{M} \sum_m^{BK} (-1)^m \rho_z(m),\end{aligned}\tag{VIII.10}$$

and their complex conjugates. These derivatives vanish when all the dynamical variables are zero, i.e. the dynamical variables are defined relative to a stationary point of the energy. Finally, the derivatives with respect to the nuclear momenta are

$$\frac{\partial E}{\partial P_z(m)} = \frac{P_z(m)}{M_n}.\tag{VIII.11}$$

The four coupled equations of motion are

$$\begin{aligned}i\frac{dz_{\pm k}}{dt} &= \frac{\partial E}{\partial z_{\pm k}^*}; \quad -i\frac{dz_{\pm k}^*}{dt} = \frac{\partial E}{\partial z_{\pm k}}, \\ \frac{d\rho_z(m)}{dt} &= \frac{\partial E}{\partial P_z(m)}; \quad -\frac{dP_z(m)}{dt} = \frac{\partial E}{\partial \rho_z(m)}.\end{aligned}\tag{VIII.12}$$

Introducing the normal coordinates (VI.7) the latter two equations become

$$\frac{dQ(k, t)}{dt} = \frac{P(k, t)}{M_n}\tag{VIII.13}$$

and

$$\begin{aligned}\frac{dP(k, t)}{dt} &= e(k)Q(k, t) \\ &\quad - 2i\delta_{k, \pi/a} \sqrt{\frac{M_n}{M}} \sum_l^{LZ} \beta_s(l) \{(z_{+l} + z_{-l}) - (z_{+l}^* + z_{-l}^*)\}\end{aligned}\tag{VIII.14}$$

with

$$e(k) = \frac{2}{a^3} \sum_{n \neq 0}^{BK} \frac{e^{-ikan}}{|n|^3} - A_{zz} - 2 \sum_{n \neq 0}^{BK} D_0(0, n) \beta_{zz}^0(0, n) e^{-ikan}.\tag{VIII.15}$$

Thus, the forces (VIII.10) become

$$\begin{aligned}\frac{\partial E}{\partial z_{+k}} &= 2A_0q + \gamma(0)q_- - 2B(k)z_{+k}^* + 2i\beta_s(k)Q(\pi/a, t)/\sqrt{MM_n} \\ \frac{\partial E}{\partial z_{-k}} &= 2A_0q + \gamma(0)q_+ - 2B(k)z_{-k}^* + 2i\beta_s(k)Q(\pi/a, t)/\sqrt{MM_n}\end{aligned}\tag{VIII.16}$$

and their complex conjugates. The equations of motion then become

$$\begin{aligned} i\frac{dz_{+k}}{dt} &= 2A_0q + \gamma(0)q_- - 2B(k)z_{+k} - 2i\beta_s(k)Q(\pi/a, t)/\sqrt{MM_n} \\ i\frac{dz_{-k}}{dt} &= 2A_0q + \gamma(0)q_+ - 2B(k)z_{-k} - 2i\beta_s(k)Q(\pi/a, t)/\sqrt{MM_n} \end{aligned} \quad (\text{VIII.17})$$

and their complex conjugates. In this particular model only the normal coordinate $Q(\pi/a, t)$ couples to the electronic motion. The other normal coordinates satisfy

$$M_n \frac{d^2 Q(k, t)}{dt^2} = e(k)Q(k, t), \quad k \neq \pi/a, \quad (\text{VIII.18})$$

with the solutions $Q(k, t) = Q_0(k)e^{-i\omega(k)t}$, with the frequencies given by

$$\omega^2(k) = -e(k)/M_n. \quad (\text{VIII.19})$$

This is the same expression as for the longitudinal frequencies in (VI.10). The longitudinal frequency in (VIII.19) can be expressed as

$$\omega^2(k) = \frac{1}{M_n} \left[-\frac{4}{a^3} \sum_{n=1}^{M/2-1} \frac{\cos(kan)}{n^3} + A_{xx} + 2 \sum_{n=1}^{M/2-1} D_0(0, n)\beta_{xx}^0(0, n) \cos(kan) \right]. \quad (\text{VIII.20})$$

Correct behavior at small k , i.e. for $\omega(k) \rightarrow 0$ requires that

$$-\frac{4}{a^3} \sum_{n=1}^{M/2-1} \frac{1}{n^3} + A_{xx} + 2 \sum_{n=1}^{M/2-1} D_0(0, n)\beta_{xx}^0(0, n) = 0. \quad (\text{VIII.21})$$

Comparison of (VII.25) with (VIII.17) shows that the difference variable $u_k = z_{+k} - z_{-k}$ still satisfies (VII.26) as in the case with frozen nuclei. Thus, obviously

$$z_{+k} - z_{-k} = u_k^* e^{-i\omega_1(k)t} + \sum_l^{LZ} X_{kl} v_l e^{i\omega_1(l)t}, \quad (\text{VIII.22})$$

as in (VII.37). Introducing the abbreviated notations

$$\begin{aligned} Q &= Q(t) = Q(\pi/a, t)/\sqrt{MM_n} \\ P &= P(t) = P(\pi/a, t)/\sqrt{MM_n} \end{aligned} \quad (\text{VIII.23})$$

straightforward algebra using (VIII.17) gives

$$i\frac{dg_k}{dt} = (4A_0 + \gamma(0))q - 2B(k)g_k - 4i\beta_s(k)Q \quad (\text{VIII.24})$$

for the sum variable $g_k = z_{+k} + z_{-k}$. The definition of q in equations (VII.15) and (VII.16) leads to the expression

$$i\frac{dg_k}{dt} = \frac{A}{2} \sum_l^{LZ} (g_l + g_l^*) - 2B(k)g_k - 4i\beta_s(k)Q, \quad (\text{VIII.25})$$

with $A = (8A_0 + 2\gamma(0))/M$. This means that the real, g_{rk} , and imaginary, g_{ik} , parts of g_k satisfy

$$\dot{g}_{rk} = -2B(k)g_{ik} - 4\beta_s(k)Q \quad (\text{VIII.26})$$

and

$$\dot{g}_{ik} = -A \sum_l^{LZ} g_{rl} + 2B(k)g_{rk}. \quad (\text{VIII.27})$$

These equations combined with

$$\begin{aligned} \dot{Q} &= \frac{1}{M_n} P \\ \dot{P} &= e(\pi/a)Q + \frac{4}{M} \sum_l^{LZ} \beta_s(l)g_{il} \end{aligned} \quad (\text{VIII.28})$$

yield in matrix canonical form

$$\begin{bmatrix} \dot{Q} \\ \dot{g}_i \\ \dot{P} \\ \dot{g}_r \end{bmatrix} = \begin{bmatrix} 0 & 0 & M_n^{-1} & 0 \\ 0 & 0 & 0 & -A + 2B \\ e(\pi/a) & b & 0 & 0 \\ -Mb^\dagger & -2B & 0 & 0 \end{bmatrix} \begin{bmatrix} Q \\ g_i \\ P \\ g_r \end{bmatrix}, \quad (\text{VIII.29})$$

with b a row matrix with elements $4\beta_s(l)/M$. The matrix A is the analog of the matrix in (VII.29) with the constant A and B is the diagonal matrix in (VII.30). This is really a partitioned problem, i.e.

$$\begin{bmatrix} \dot{Q} \\ \dot{g}_i \end{bmatrix} = \begin{bmatrix} M_n^{-1} & 0 \\ 0 & -A + 2B \end{bmatrix} \begin{bmatrix} P \\ g_r \end{bmatrix} \quad (\text{VIII.30})$$

and

$$\begin{bmatrix} \dot{P} \\ \dot{g}_r \end{bmatrix} = \begin{bmatrix} e(\pi/a) & b \\ -Mb^\dagger & -2B \end{bmatrix} \begin{bmatrix} Q \\ g_i \end{bmatrix}. \quad (\text{VIII.31})$$

Differentiating (VIII.30) with respect to the time parameter and using (VIII.31) one obtains

$$\begin{bmatrix} \ddot{Q} \\ \ddot{g}_i \end{bmatrix} = \begin{bmatrix} e(\pi/a)/M_n & b/M_n \\ M(A - 2B)b^\dagger & 2(A - 2B)B \end{bmatrix} \begin{bmatrix} Q \\ g_i \end{bmatrix} = F \begin{bmatrix} Q \\ g_i \end{bmatrix}. \quad (\text{VIII.32})$$

This nonhermitian problem can be brought to classical canonical form by a similarity transformation $A = L^{-1}FL$ i.e. the resulting matrix A consists of Jordan blocks

$$[\Lambda_j], \begin{bmatrix} \Lambda_k & 1 \\ 0 & \Lambda_k \end{bmatrix}, \begin{bmatrix} \Lambda_l & 1 & 0 \\ 0 & \Lambda_l & 1 \\ 0 & 0 & \Lambda_l \end{bmatrix}, \dots \quad (\text{VIII.33})$$

For the case where all the Jordan blocks are one-dimensional, the matrix A is diagonal. Then, defining a new column matrix

$$f_i = L^{-1} \begin{bmatrix} Q \\ g_i \end{bmatrix} \quad (\text{VIII.34})$$

the equation of motion can be expressed as

$$\frac{d^2 f_i}{dt^2} = \Lambda f_i. \quad (\text{VIII.35})$$

The negative of the eigenvalues of Λ are then the frequencies squared of the coupled system of electrons and nuclei. The requirement that the frequencies be real puts further constraints on the parameters in the matrices A , B , and b . For small vibrations around the ground state all frequencies should be real.

IX. Conclusions

The END theory, which provides a fully dynamical treatment of electrons and nuclei without resorting to the common Born-Oppenheimer or Adiabatic approximations, has been used to formulate an internally consistent description of electrons and vibrating nuclei of an extended system. In order to demonstrate the essential features of such a system, allowing for the coupling between nuclear and electronic dynamics, a PPP-like hamiltonian is employed. Such a hamiltonian yields a total energy that scales properly with the size of the system and exhibits a physically correct dependence on small nuclear displacements. It also satisfies the primary requirement of all treatments of extended electronic systems, namely permitting a proper treatment of the long range nature of the Coulomb interaction.

The nuclei are treated classically and the electrons are described by a single determinantal wavefunction built with complex spin orbitals. The nuclear positions and conjugate momenta are the dynamical variables of the nuclear dynamics, while the electronic dynamical variables are the complex coefficients mixing Bloch functions below with those above the Fermi level. The Wannier functions (or corresponding Bloch functions) in one band associated with the equilibrium nuclear positions make up the electronic basis. The particular sample system studied is metallic with a half-filled band in its reference state.

The equations that govern the time evolution of the dynamical variables are derived via the time-dependent variational principle. Their analysis is presented in three steps. First, frozen electronic degrees of freedom lead to a variant derivation of the classical equations of motion of vibrating nuclei. Second, frozen nuclear degrees of freedom yield a RPA description of the electronic excitations. Third, the full END equations are solved revealing that the highest frequency nuclear mode is the only one coupling to the electron dynamics.

In spite of its simplicity, a linear chain with one atom per unit cell and a single valence electron per atom exhibits the essential complexities to demonstrate the generality of the approach, yet permits a straightforward and relatively uncluttered analysis. Additional specializations include the detailed treatment of only longitudinal vibrations and the selection of only one mixing coefficient per occupied spin orbital linking it to a single virtual spin orbital as is done in the alternant molecular orbital AMO method.

Permitting a detailed and transparent application of the theory to an extended system these simplifications in no way reflect any basic limitations of the END approach. As is indicated in sections IV and VI transverse vibrations follow in exactly the same manner as in traditional treatments. Similarly, systems with more than one atom per unit cell involve more work, but no additional conceptual challenges. Also, the consideration of several electronic mixing coefficients leads to more dynamical equations, but no significantly different behavior from that of the simple AMO choice. Inclusion of more than one energy band again means more work but adds nothing fundamentally new.

Extensions of the simplest END model to one with quantum nuclei and possibly also a multiconfigurational electronic description have been accomplished for finite molecular systems and might also be attempted for extended systems. In particular, a quantum mechanical treatment of the nuclei is necessary to permit a discussion of phonon systems and a study of electron-phonon coupling.

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